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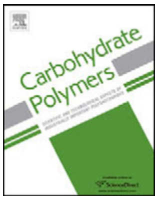

Synthesis and characterization of graft copolymers of *N*-Vinyl-2-Pyrrolidone onto guar gum for sorption of Fe^{2+} and Cr^{6+} ions

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ABSTRACT

To develop low cost and environment friendly technologies for removal of metal ions from water systems, graft copolymers based on guar gum and poly(*N*-Vinyl-2-Pyrrolidone) were synthesized. The optimum reaction conditions were evaluated for grafting by varying nature and amount of solvent, change in concentration of monomer and initiator, reaction time and temperature. Graft copolymers were characterized by FTIR, SEM, XRD, thermal analysis and swelling studies. Sorption of Fe^{2+} and Cr^{6+} ions on graft copolymers was investigated as a function of percent grafting, change in metal ion concentration and temperature to define their end-uses in separation technologies.

1. Introduction

The modification of polymers has received much attention recently. Among the methods of modification of polymers, grafting is one of the promising methods to impart a variety of functional groups to a polymer. Literature survey reveals that recently a good amount of work has been carried out on grafting of various vinyl monomers onto various backbone polymers using different initiating systems (Al-Karawi, Ai-Qaisi, Abdullah, Al-Mokaram, & Al-Heetimi, 2011; Carreira, Gonçalves, Mendonça, Gil, & Coelho, 2010; Kumar, Singh, & Ahuja, 2009; Saboktakin, Maharramov, & Ramazanov, 2009; Sand, Yadav, & Behari, 2010; Sharma & Mishra, 2010; Singh, Chauhan, Kumar, & Chauhan, 2007; Singha & Rana, 2010; Ye et al., 2010; Zhang et al., 2009). Guar gum is a high molecular weight hydrocolloidal hetero-polysaccharide composed of galactan and mannan units. Guar gum has been modified by derivatization, grafting and network formation to improve its property profile for a wide spectrum of end-uses. Using different initiating systems grafting of methacrylamide (Behari, Kumar, Tripathi, & Pandey, 2001), acrylonitrile (Trivedi, Kalia, Patel, & Trivedi, 2005), acrylic acid (Li, Wu, Wang, & Duan, 2006; Pandey, Srivastava, Tripathy, & Behari, 2006) and acrylamide (Singh, Tiwari, Tripathi, & Sanghi, 2004) onto guar gum has been reported. Grafting of acrylamide onto guar gum has been applied to carry out using high-energy Co^{60} γ-radiation (Biswal et al., 2007) to enhance its flocculating properties for industrial effluents. Graft copolymers of 4-vinyl pyridine with partially carboxymethylated guar gum were synthesized using a bromate/thiourea redox pair (Tripathy, Mishra, Srivastava, Mishra, & Behari, 2008), graft copolymers showed enhancement in metal ion uptake and flocculation behaviour than substrate. Acryloyl guar gum (AGG) and its hydrogel materials were synthesized (Thakur, Chauhan, & Ahn, 2009) for their use as carriers and slow release devices of two pro-drugs, L-tyrosine and 3,4-dihydroxy phenylalanine (L-DOPA). Poly(acrylamide) modified guar gum–silica nanocomposites has been reported (Singh, Pandey, Singh, & Sanghi, 2009) for removal of cadmium from aqueous solutions by adsorption process. Poly(methylacrylate) was grafted on to guar gum using persulfate/ascorbic acid redox pair (Singh, Kumari, Pandey, & Narayan, 2009), and sorption conditions were optimized for the removal of Cr(VI) ions. Hydrogels based on guar gum were synthesized after partial hydrolysis/depolymerization and crosslinking with *N*,*N*-methylenebisacrylamide (Chauhan, Chauhan, & Ahn, 2009) for sorption of Cu^{2+} ions.

In the present work, we have synthesized graft copolymers of guar gum and poly(*N*-Vinyl-2-Pyrrolidone) (VP) using potassium persulphate (KPS) and ferrous ammonium sulphate (FAS) as redox pair initiator. The optimum reaction conditions were evaluated for grafting by varying nature and amount of solvent, change in concentration of monomer and initiator, reaction time

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and temperature. Sorption of Fe^{2+} and Cr^{6+} ions on graft copolymers was investigated as a function of percent grafting, change in metal ion concentration and temperature to define their end-uses in separation technologies.

2. Experimental

2.1. Materials and methods

Guar gum (Lucid Colloids, Jodhpur, India) and *N*-Vinyl-2-Pyrrolidone (Merck, Germany) potassium persulphate (KPS) (Ranbaxy, SAS Nagar, India) and ferrous ammonium sulphate (FAS) (CDH, New Delhi, India) were used as received. All the chemicals used were of analytical grade.

2.2. Graft copolymerization

The optimum grafting reaction conditions for grafting of *N*-Vinyl-2-Pyrrolidone (VP) were obtained by free radical mechanism using KPS and FAS as redox pair initiator (Sharma, Lalita, Chauhan, & Verma, 2010). Five different solvents were used in which calculated amount of VP, FAS, KPS were added at 60 °C for 1 h for grafting of VP onto 1 g of guar gum. Maximum grafting was observed in water. Then amount of water was varied and grafting reaction scheme was designed as one parameter was varied (i.e. concentration of initiator or concentration of monomer or reaction time or reaction temperature) for a set of reaction keeping other reaction parameters constant (Table 1) to obtain optimum grafting conditions on to 1 g of guar gum. The grafted sample has been precipitated out by pouring it into water/methanol mixture. The grafted sample has been separated by filtration, dried and weighed. Poly(*N*-Vinyl-2-Pyrrolidone) remained in the filtrate. The percent grafting (P_g) and percent grafting efficiency (*%GE*) were calculated which can be expressed as (Chauhan, Lal, Sharma, Sarwade, & Guleria, 2002):

$$P_g = \frac{\text{Weight of graft copolymer} - \text{weight of polymer backbone}}{\text{Weight of polymer backbone}} \times 100$$

$$\%GE- = \frac{\text{Weight of graft copolymer} - \text{weight of polymer backbone}}{\text{Weight of monomer charged}} \times 100$$

2.3. Characterization of graft copolymers

Characterization of guar gum and its graft copolymers were done by FTIR, XRD, SEM, thermal analysis and swelling studies. FTIR spectra of guar gum and its graft copolymers were recorded using Thermo Nicolet (Model 6700) spectrometer in KBr pellets. Scanning Electron Micrographs were taken on Jeol, JSM-6100 at an accelerating voltage of 20 kV. X-ray diffraction studies were carried out using X'Pert PRO (PAN analytical, Netherlands), Rigaku RotaFlex operating with Cu Kα radiation, 45 kV, 40 mA and equipped with a graphite monochromator. Thermal analysis was done on Shimadzu DTG-60; simultaneous TG/DT model. Swelling studies were carried out on guar gum graft copolymers in which 100 mg of the copolymer was taken in 20.00 mL of water. Surface water on the swollen polymer was removed by softly pressing between the folds of filter paper and increase in weight was recorded. Percent swelling (P_s) was calculated by the following expression (Chauhan, Chauhan, Chauhan, Kumar, & Kumari, 2007).

$$P_s = \frac{\text{Weight of the swollen polymer} - \text{weight of dry polymer}}{\text{Weight of dry polymer}} \times 100$$

2.4. Metal ion sorption

Sorption of Fe^{2+} and Cr^{6+} ions has been studied by equilibration method on graft copolymers of guar gum with poly(VP). Graft copolymers were checked for their sorption behaviour at variable conditions of P_g, change in ionic strength and temperature. 0.025 g of guar gum and graft copolymers with different P_g were studied for ion sorption studies by immersion for 60 min in 25.00 mL aqueous solutions of metal ions of known concentration. They were filtered after 60 min. Metal ions from filtrate were analyzed for concentration of rejected ions on DR 2010 spectrophotometer (Hach, Co., USA) using standard pillow reagents. The spectrophotometer has high sensitivity with maximum limits of 3.0 mg/L and 0.6 mg/L, respectively, of Fe^{2+} and Cr^{6+} ions. Thus, the residual filtrate was diluted to reach this range. All weights were taken on Denver TR-203 Balance having minimum readability of 1.0 mg. Different relationships were used to express sorption behaviour (Chauhan, Singh, Chauhan, Verma, & Mahajan, 2005), i.e. percent uptake (P_u), partition coefficient (K_d) and retention capacity (Q_r):

$$P_u = \frac{\text{Amount of total ions in feed} - \text{Amount of ions rejected}}{\text{Amount of total ions in feed}} \times 100$$

$$K_d = \frac{\text{Amount of metal ions in the polymer}}{\text{Amount of metal ions left in the solution}} \times \frac{\text{Volume of solution (mL)}}{\text{Weight of dry polymer (g)}}$$

$$Q_r = \frac{\text{Amount of metal ions in the polymer (mEq)}}{\text{Weight of dry polymer (g)}}$$

3. Results and discussion

3.1. Effects of reaction parameters on grafting of VP onto guar gum

Optimum reaction conditions for grafting of VP onto guar gum were carried out using KPS and FAS as redox pair initiators. Effects of various reaction parameters on P_g and *%GE* of VP onto guar gum have been investigated and results are discussed.

3.1.1. Effect of nature and amount of solvent system

Solvents play important role in determining $P_{g.}$ Solvent affects graft yield in many ways. Swelling of backbone polymer by solvent helps in better diffusion of monomer to the backbone polymer and also enhances diffusion of growing monomer macro-radicals. Chain transfer reactions of solvent affect not only graft yield but also size of graft chains and mechanism of grafting. Further, solvent interacts not only with the backbone polymer but also with initiator system and monomer and such interactions are also important factor that determines graft yield. In the present study, effects of solvents such as acetone, benzene, dioxane, MeOH and water on P_g and *%GE* were studied in 10.00 mL of these solvents keeping other reaction conditions constant. The order of P_g in these solvents can be presented as acetone < dioxane < benzene < carbon tetrachloride < water. Similar order was recorded in case of %GE. The lower P_g and *%GE* in organic solvents have been observed despite the fact that KPS/FAS is not soluble in these solvents under the employed reaction conditions. Solubilization requirements of the initiator play important role to increase grafting. Maximum 27.30% P_g and 26.199%*GE* were observed in water (Table 1).

Amount of water was varied in the range 10.00–30.00 mL and appreciable changes in the graft yield have been observed. The optimum value of P_g 60.20 and *%GE* 57.773 were reported at 15.00 mL water (Table 1). With higher dilution of reaction system results in

Table 1
Effect of reaction conditions on graft copolymerization of VP onto guar-gum.[a]

S. no.	Solvent	Amount of solvent (mL)	Conc. of monomer [VP] mol/L × 10^{-2}	Initiator concentration mol/L × 10^{-2} *KPS*	*FAS*	Time (h)	Temp (°C)	Percent grafting (P_g)	Grafting efficiency *%GE*
1	H_2O	10	93.87	500.0	482.1	1.00	60	27.30	26.199
2	Benzene	10	93.87	500.0	482.1	1.00	60	19.08	18.311
3	Dioxane	10	93.87	500.0	482.1	1.00	60	15.39	14.769
4	CCl_4	10	93.87	500.0	482.1	1.00	60	24.13	23.157
5	Acetone	10	93.87	500.0	482.1	1.00	60	9.90	9.501
6	H_2O	15	62.58	333.3	321.4	1.00	60	60.20	57.773
7	H_2O	20	46.93	250.0	241.0	1.00	60	48.60	46.641
8	H_2O	25	37.55	200.0	192.8	1.00	60	17.00	16.314
9	H_2O	30	31.29	166.6	160.7	1.00	60	6.73	6.458
10	H_2O	15	62.58	333.3	321.4	1.00	60	60.2	57.773
11	H_2O	15	93.87	333.3	321.4	1.00	60	117.0	74.856
12	H_2O	15	125.17	333.3	321.4	1.00	60	162.4	77.927
13	H_2O	15	156.46	333.3	321.4	1.00	60	168.0	64.491
14	H_2O	15	156.46	666.6	321.4	1.00	60	96.33	36.429
15	H_2O	15	156.46	1000.0	321.4	1.00	60	100.5	38.579
16	H_2O	15	156.46	1333.3	321.4	1.00	60	75.2	28.867
17	H_2O	15	156.46	1666.6	321.4	1.00	60	8.76	3.363
18	H_2O	15	156.46	333.3	642.8	1.00	60	129.0	49.520
19	H_2O	15	156.46	333.3	964.2	1.00	60	78.9	30.287
20	H_2O	15	156.46	333.3	1285.7	1.00	60	9.59	3.681
21	H_2O	15	156.46	333.3	321.4	1.00	60	168.0	64.491
22	H_2O	15	156.46	333.3	321.4	1.5	60	38.0	14.567
23	H_2O	15	156.46	333.3	321.4	2.0	60	30.4	11.669
24	H_2O	15	156.46	333.3	321.4	2.5	60	12.9	4.952
25	H_2O	15	156.46	333.3	321.4	3.0	60	9.41	3.612
26	H_2O	15	156.46	333.3	321.4	1.0	70	23.83	9.148
27	H_2O	15	156.46	333.3	321.4	1.0	80	16.40	6.296
28	H_2O	15	156.46	333.3	321.4	1.0	90	15.39	5.908
29	H_2O	15	156.46	333.3	321.4	1.0	100	14.41	5.532

[a] Guar gum = 1 g.

sharp decrease in P_g and *%GE* as accessibility of reacting species to both monomer and backbone polymer was diminished.

3.1.2. *Effect of monomer and initiator concentration*

The concentration of monomer (VP) was varied from 62.58×10^{-2} mol/L to 156.46×10^{-2} mol/L at optimum solvent composition and optimum KPS and FAS concentration 333.3×10^{-2} mol/L and 321.4×10^{-2} mol/L. With the increase in monomer concentration a regular increase in graft was observed. Optimum P_g of 168.0 was recorded at 156.46×10^{-2} mol/L of VP concentration and 64.491*%GE* was observed at this VP concentration (Table 1).

It follows from Table 1 that with increase of KPS and FAS concentration from 333.3×10^{-2} mol/L to 1666.6×10^{-2} mol/L and FAS concentration from 321.4×10^{-2} mol/L to 1285.7×10^{-2} mol/L, decrease in both P_g and *%GE* is observed. At higher initiator concentrations fall in the graft yields is observed because it enhances the chances of more homopolymer formation.

3.1.3. *Effect of reaction time and temperature*

Effect of variation of reaction time studied from 1 h to 3 h. Maximum P_g 168.0 and maximum *%GE* 64.491 were reported at 1.0 h reaction time (Table 1) at 60 °C temperature, 333.3×10^{-2} mol/L of KPS, 321.4×10^{-2} mol/L of FAS and 156.46×10^{-2} mol/L of VP.

Temperature plays important role in polymerization processes by acceleration of decomposition of initiator, enhanced mobility of monomer molecules and diffusion to the polymer backbone. Temperature was varied form 60 °C to 100 °C at the evaluated optimum reaction parameters discussed above. Grafting at different temperatures was observed to follow the order 60 °C > 70 °C > 80 °C > 90 °C > 100 °C (Table 1). Thus, there exists an optimum temperature to afford maximum graft yield, below this temperature decomposition of initiator and diffusion processes are not adequate to yield high graft levels. Optimum P_g (168.0) and *%GE* (64.491) were observed at 60 °C.

4. Evidence of grafting

Characterization of guar gum and its graft copolymers was done to give important information of grafted polymers and structural differences between backbone and graft copolymers.

4.1. *FTIR analysis*

FTIR of guar gum show broad peaks at 3217.2 cm^{-1} (O–H stretching), this broad band indicates association due to –OH groups (Fig. 1a). Other important peaks are observed at 1156.5, 1093.9, 1020.2 cm^{-1} which are due to C–O–C stretching from glycosidic linkages and O–H bending from alcohols. On grafting of *N*-Vinyl-2-Pyrrolidone, IR bands have been witnessed due to characteristic functional groups incorporated onto guar gum apart from the above listed bands (Fig. 1b). FTIR of graft copolymer show peak at 1664.1 (C═O stretching) while another distinguished peak at 1289.9 (C–N stretching for secondary amide) is witnessed, which are characteristics of the monomeric functionalities. Additional product formation is confirmed by disappearance of O–H bending vibration indicating the mechanism of O–H side grafted reaction. This FTIR analysis indicates that *N*-Vinyl-2-Pyrrolidone was grafted onto guar gum.

4.2. *Scanning electron microscopy*

Scanning electron micrographs (SEM) of ungrafted guar gum and grafted copolymers are presented in Fig. 2. The ungrafted guar gum particles are small having rough surface morphology. Surface of grafted sample clearly indicates the morphological changes brought about by grafting as deposits of the graft copolymers are seen clearly as compared to the continuous surface of the backbone.

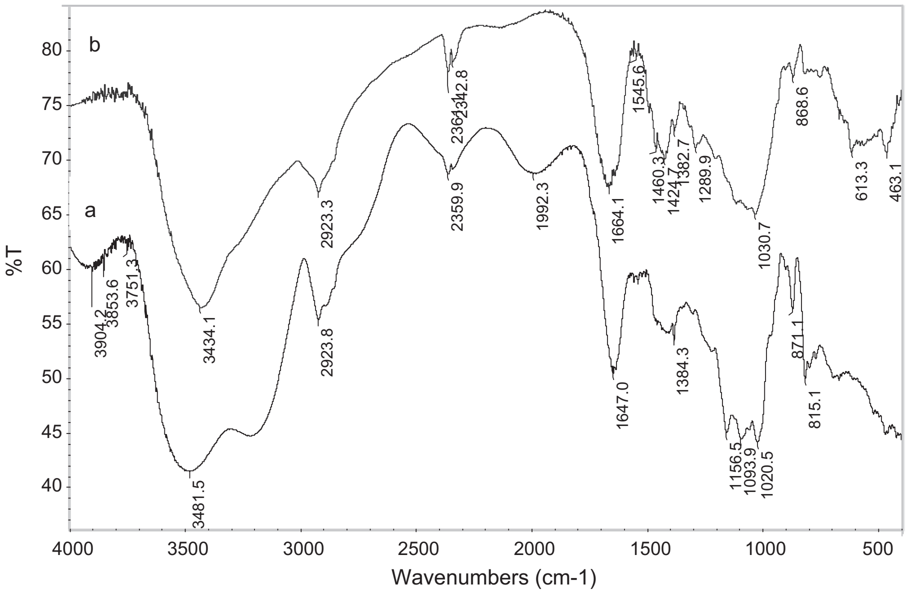

Fig. 1. FTIR of (a) ungrafted guar gum and (b) grafted guar gum.

4.3. Thermal analysis

Two-stage decomposition for ungrafted guar gum is observed. Guar gum degrades mainly by dehydration and depolymerization. The degradation in temperature range of 49.79–166.06 °C (Fig. 3a) with a loss of 14.291%, is because of dehydration. Decomposition curve showed that second stage of degradation starts at 252.15 °C and lasts up to 784.15 °C with a total weight loss of 69.707%. The sample begins to decompose at 252.15 °C and rapidly loses 55.279% of its weight up to 374.95 °C. This is caused by sequence of processes in which galactose and mannose cleave from the guar gum backbone and then decomposition occurs. Beyond 374.95 °C, the weight loss is slow and gradual up to 784.15 °C leaving 16.002% residual weight. The ungrafted guar gum is stable in 166.06–252.15 °C temperature range. Grafted guar gum shows a two stage decomposition which starts from 43.80 °C to 168.59 °C and 168.59 °C to 796.63 °C with a weight loss of 80.999% (Fig. 3b). Decomposition is very fast from 168.59 to 290.19 with 42.785% loss in weight.

Many important exothermic and endothermic peaks are observed in differential thermal analysis (DTA) of normal and grafted Guar gum. A number of exothermic peaks at 44.08, 216.24 and 366.38 have been observed in DTA curve of ungrafted guar gum. Where as in case of grafted sample the exothermic peaks are observed at 53.36,197.73, 288.82. Two endothermic peaks at 119.14 and 453.28 are observed in DTA curve of ungrafted guar gum while in case of grafted guar gum endothermic peaks were observed at 128.51, 252.39, 357.14 and 456.42. Out of which the endothermic peaks at 252.39 and 357.14 can be because of decomposition of amide group attached to guar gum.

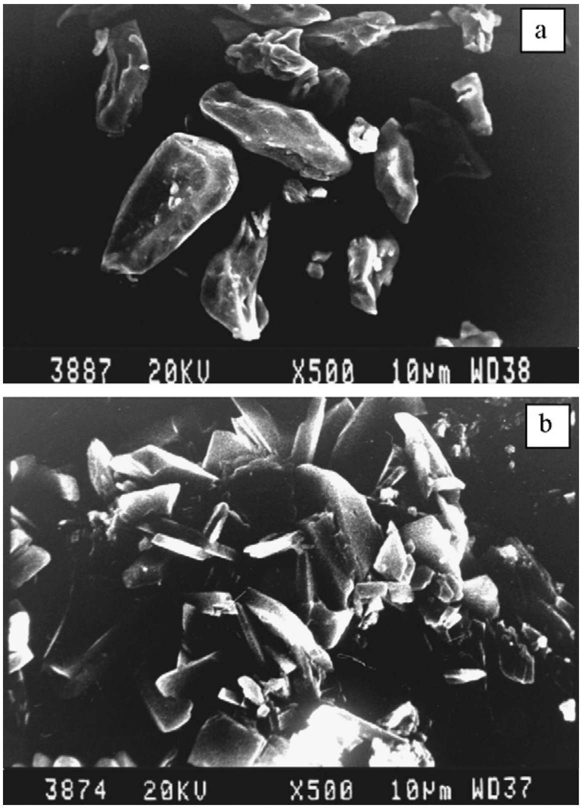

Fig. 2. SEM of (a) ungrafted guar gum and (b) grafted guar gum.

4.4. XRD analysis of guar gum and its graft copolymers

X-ray diffraction data collection was recorded in the range of $2\theta = 20–80°$ with a step size of 0.0170°. XRD curve of ungrafted guar gum shows the overall amorphous region (Fig. 4a), but in XRD curve of grafted sample a number of peaks are observed at 2θ positions at 22.0003, 24.1790, 30.1402, 31.2579, 37.4152, 43.6750 with relative intensities of 100.00, 17.18, 33.54, 50.51, 12.82, 11.34 respectively (Fig. 4b) which confirms the increase in crystallinity in polymer because of grafting. Singh, Kumari, et al. (2009) have also reported the increase in crystalline character of grafted guar gum.

4.5. Swelling study

Swelling studies of GG-*g*-poly(VP) were carried in water at room temperature. On grafting, guar gum matrix opens up considerably where diffusion of the solvent takes place. GG-*g*-poly(VP)

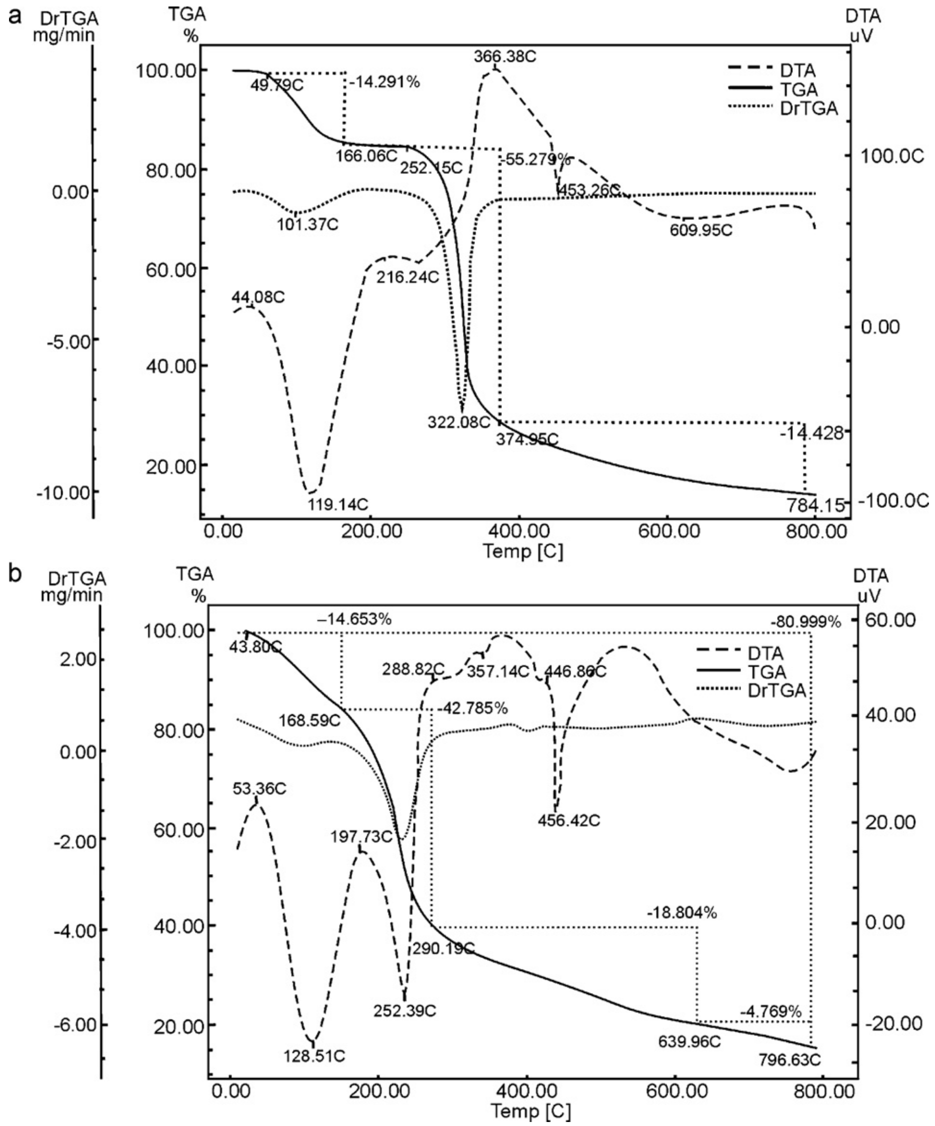

Fig. 3. TGA/DTA of (a) ungrafted guar gum and (b) grafted guar gum.

synthesized under different set of reaction conditions i.e. change in reaction in time, change in monomer concentration, change in KPS concentration, change in FAS concentration and optimum percent grafting samples with P_g of 38.0, 60.2, 100.5, 129.0 and 168.0 respectively were subjected to swelling studies. Percent swelling (P_s) of graft copolymers is reported very high within 2 h but after 4 h the increase P_s is not very high and it is almost constant after 24 h (Table 2) as graft copolymers form gels by absorbing water. Thus it is evident that swelling behaviour in water is more a function of opening of graft copolymer.

5. Mechanism of graft copolymerization

On the basis of above discussion free radical mechanism using KPS and FAS as redox pair initiator, for grafting of *N*-Vinyl-2-Pyrrolidone onto guar gum has been proposed. Dissociation of initiator gives $SO_4^{-\bullet}$ and $^\bullet OH$ free radicals. These radicals abstract hydrogen atom from guar gum producing macro radicals (GG–O$^\bullet$). The monomer molecules also converted into free radicals by initiator and the combine with guar gum as shown in propagation steps (Fig. 5). In this way grafted chains grow and terminated by

Table 2
Swelling study of graft copolymers in water.

S. no.	Percent grafting (P_g)	Percent swelling (P_s)		
		After 2 h	After 4 h	After 24 h
1.	0.00	354	395	406
2.	38.0	383	411	423
3.	60.2	427	488	490
4.	100.5	390	445	485
5.	129.0	470	520	543
6.	168.0	496	592	617

Graft copolymer = 100 mg, amount of water = 20 mL, temperature = 25 °C.

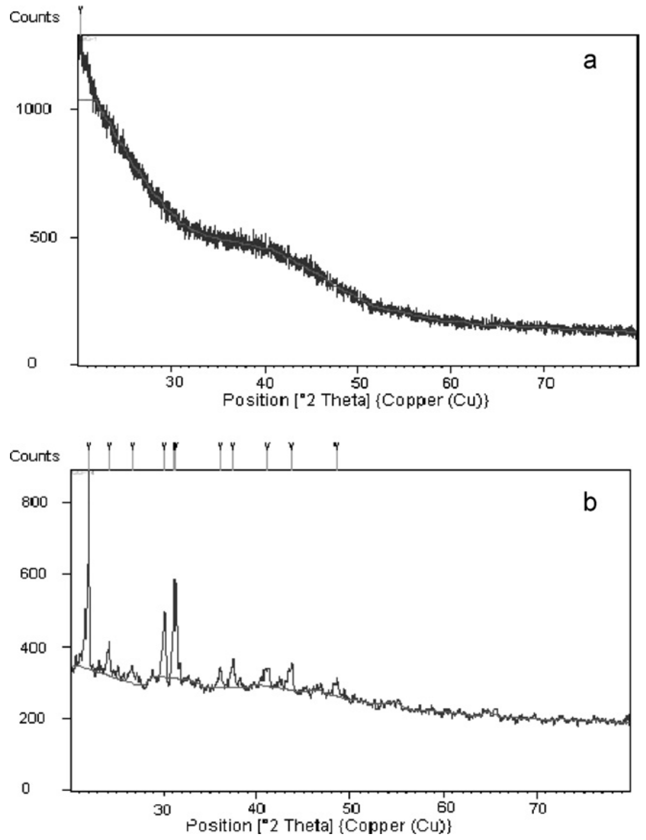

Fig. 4. XRD curve of (a) ungrafted guar gum and (b) grafted guar gum.

coupling to give graft copolymer and homopolymer. The probable mechanism can be represented as:

Initiation:

$$Fe^{2+} + O_3{}^{-}S–O–O–SO_3{}^{-} \rightarrow Fe^{3+} + SO_4{}^{2-} + SO_4{}^{-\bullet} \quad (1)$$

$$SO_4{}^{-\bullet} + H_2O \rightarrow HSO_4{}^{-} + {}^{\bullet}OH \quad (2)$$

$$GG–OH + SO_4{}^{-\bullet} \rightarrow GG–O^{\bullet} + HSO_4{}^{-} \quad (3)$$

$$GG–OH + {}^{\bullet}OH \rightarrow GG–O^{\bullet} + H_2O \quad (4)$$

$$M + {}^{\bullet}OH \rightarrow {}^{\bullet}M–OH \quad (5)$$

$$M + SO_4{}^{-\bullet} \rightarrow {}^{\bullet}M–SO_4{}^{2} \quad (6)$$

$$M + GG–O^{\bullet} \rightarrow GG–OM^{\bullet} \quad (7)$$

Propagation:

$$GG–OH + {}^{\bullet}M–OH \rightarrow {}^{\bullet}GG–M–OH \quad (8)$$

$${}^{\bullet}GG–M–OH + nM \rightarrow GG–(M)^{\bullet}{}_{n+1}–OH \quad (9)$$

$$GG–O^{\bullet} + nM \rightarrow GG–(M)_n{}^{\bullet} \quad (10)$$

$${}^{\bullet}M–OH + nM \rightarrow HO–(M)_n–M^{\bullet} \quad (11)$$

Termination:

$$GG–(M)^{\bullet}{}_{n+1} + GG–(M)^{\bullet}{}_{n+1} \rightarrow GG–(M)_{2n+2}–GG(\text{graft copolymer}) \quad (12)$$

$$GG–(M)_n–M^{\bullet} + Fe^{3+} \rightarrow GG–(M)_{n+1} + Fe^{2+} \quad (13)$$

$$GG–(M)_n–M^{\bullet} + {}^{\bullet}OH \rightarrow GG–(M)_{n+1}–OH \quad (14)$$

Homopolymer formation

$${}^{\bullet}M–OH + nM \rightarrow HO–(M)_n–M^{\bullet}$$

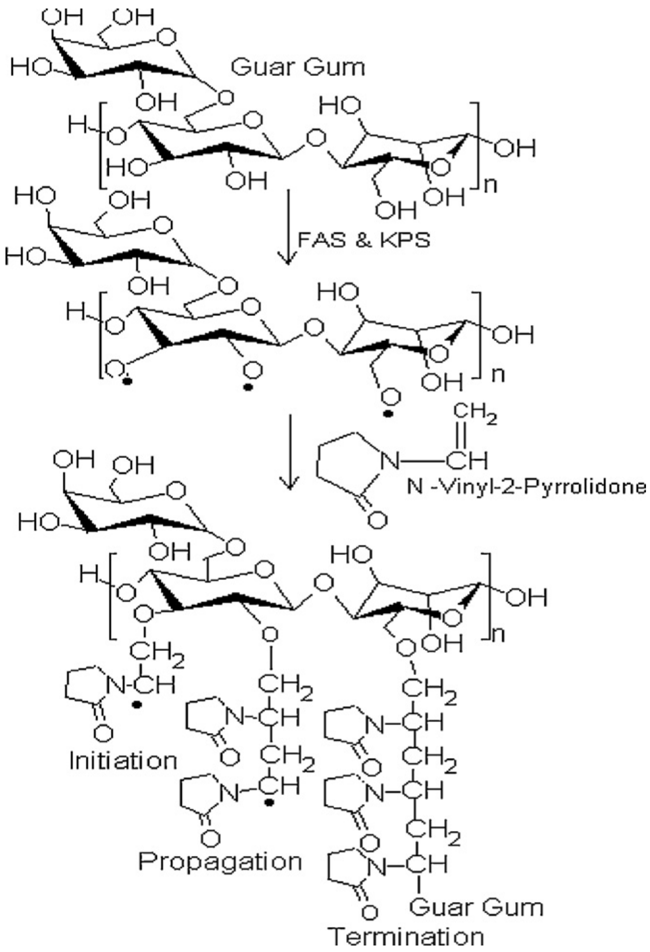

Fig. 5. Systematic representation of grafting mechanism of VP on guar gum.

$$HO–(M)_n–M^{\bullet} + GG–OH \rightarrow HO–(M)_n–MH(\text{Homopolymer}) + GG–O^{\bullet}$$

GG–OH is guar gum

M is monomer (*N*-Vinyl-2-Pyrrolidone)

6. Metal ion sorption

Polymers based upon anhydroglucose units afford active glycolic functionalities for metal ion complexation. The linkage is mainly of co-ordinate type. Hydrogels partition metal ions between solution and gel phase resulting into ion sorption. Depending on the structure of the supports, sorption is a combination of ion exchange and simple adsorption processes. The results from the sorption of Fe^{2+} and Cr^{6+} ions are discussed.

6.1. Sorption studies as function of percent grafting

Results of sorption of Cr^{6+} and Fe^{2+} ions onto guar gum and graft copolymers of guar gum are presented in Table 3. Guar gum and graft copolymers with different P_g were studied for ion sorption studies by immersion of 0.025 mg sample for 60 min in 25.00 mL solutions of Cr^{6+} and Fe^{2+} ions of 5.00 mg/L concentration at 25 °C and pH 7. In the present study, sorption of Cr^{6+} ions is not significant by any graft copolymer. Maximum percent uptake (P_u) for Cr^{6+} ions is 24.8% and 61.8% for Fe^{2+} ions is observed in sample with maximum P_g i.e. 168.0. The value of percent ion uptake (P_u), partition coefficient (K_d) and retention capacity (Q_r) first increases as the percent grafting is increased, which reaches maximum when P_g is 168

Table 3
Sorption studies of Cr^{6+} and Fe^{2+} ions on guar gum and its graft copolymers as a function of percent grafting (P_g); metal ion concentration and temperature.

S. no.	Polymer	P_g	Amount of metal ions in feed (mg/L)	Amount of metal ions sorbed (mg)	Amount of metal ions rejected (mg)	Percent ion uptake (P_u)	Partition coefficient (K_d) (g/g)	Retention capacity (Q_r) (meq/g)
Sorption of Cr^{6+} ions as a function of P_g[a]								
1.	Gaur gum		5.00	0.59	4.41	11.8	133.78	2.723
2.	GG-*g*-poly(VP)	38.0	5.00	0.61	4.36	12.2	139.91	2.816
3.	GG-*g*-poly(VP)	60.2	5.00	0.49	4.51	9.84	108.65	2.262
4.	GG-*g*-poly(VP)	100.5	5.00	0.82	4.18	16.4	196.17	3.785
5.	GG-*g*-poly(VP)	129.0	5.00	1.07	3.93	21.4	272.26	4.939
6.	GG-*g*-poly(VP)	**168.0**	**5.00**	**1.24**	**3.76**	**24.8**	**329.79**	**5.724**
Sorption of Fe^{2+} ions as a function of P_g[a]								
7.	Gaur gum		5.00	0.31	4.69	6.20	66.09	0.443
8.	GG-*g*-poly(VP)	38.0	5.00	0.33	4.67	6.6	70.66	0.471
9.	GG-*g*-poly(VP)	60.2	5.00	1.29	3.71	25.8	347.71	1.843
10.	GG-*g*-poly(VP)	100.5	5.00	1.99	3.01	39.8	661.13	2.843
11.	GG-*g*-poly(VP)	129.0	5.00	2.11	2.89	42.2	730.10	3.014
12.	GG-*g*-poly(VP)	**168.0**	**5.00**	**3.09**	**1.91**	**61.8**	**1575.92**	**4.414**
Sorption of Cr^{6+} ions as a function of change in metal ion concentration[a]								
1.	GG-*g*-poly(VP)	168.0	5.00	1.24	3.76	24.8	329.79	5.724
2.	GG-*g*-poly(VP)	168.0	25.00	6.05	18.95	24.21	319.26	27.922
3.	GG-*g*-poly(VP)	168.0	50.00	9.85	40.15	19.76	245.33	45.459
4.	GG-*g*-poly(VP)	168.0	75.00	20.70	54.30	27.63	381.26	95.534
5.	GG-*g*-poly(VP)	**168.0**	**100.00**	**29.30**	**70.70**	**29.31**	**414.43**	**135.225**
Sorption of Fe^{2+} ions as a function of change in metal ion concentration[a]								
6.	GG-*g*-poly(VP)	168.0	5.00	3.09	1.91	**61.8**	1617.80	4.414
7.	GG-*g*-poly(VP)	168.0	25.00	17.05	7.95	68.20	2245.28	24.357
8.	GG-*g*-poly(VP)	168.0	50.00	38.18	11.82	76.36	3230.12	54.543
9.	GG-*g*-poly(VP)	168.0	75.00	46.99	28.01	62.65	1677.62	67.128
10.	GG-*g*-poly(VP)	**168.0**	**100.00**	**77.33**	**22.67**	**77.33**	**3411.12**	**110.47**
Sorption of Cr^{6+} ions as a function of change in temperature[a]								
		(Temp.)						
1.	GG-*g*-poly(VP)	25	100.00	29.30	70.7	29.30	414.43	135.225
2.	GG-*g*-poly(VP)	**30**	**100.00**	**30.75**	**69.25**	**30.75**	**444.04**	**141.918**
3.	GG-*g*-poly(VP)	35	100.00	09.32	90.68	09.32	102.78	43.014
4.	GG-*g*-poly(VP)	40	100.00	06.66	93.34	06.66	71.35	30.737
5.	GG-*g*-poly(VP)	45	100.00	08.87	91.13	08.87	97.33	40.937
Sorption of Fe^{2+} ions as a function of change in temperature[a]								
6.	GG-*g*-poly(VP)	25	100.00	77.33	22.67	77.33	3411.12	110.47
7.	GG-*g*-poly(VP)	**30**	**100.00**	**78.11**	**21.89**	**78.11**	**3568.29**	**111.58**
8.	GG-*g*-poly(VP)	35	100.00	54.23	45.77	54.23	1184.84	77.89
9.	GG-*g*-poly(VP)	40	100.00	33.33	66.67	33.33	499.93	47.61
10.	GG-*g*-poly(VP)	45	100.00	30.45	69.55	30.45	437.81	43.5

[a] Solution taken = 25 mL, sample taken = 0.025 g, time = 60 min, temperature = 25 °C, pH 7.

for both metal ions. This might be due to the fact that as grafting increases, the density of sorption sites for metal ions are increased due to availability of additional functional groups of poly-pendent chain of monomer, which further increases with increased grafting. Moreover, functional group incorporated by grafting and its ability to interact with metal ion play important role in the determination of selectivity and quantum of metal ion uptake (Srivastava & Behari, 2007).

6.2. *Sorption studies as function of change in ion strength*

0.025 mg graft copolymers with maximum P_g was then subjected for sorption of Fe^{2+} and Cr^{6+} ions from their 25.00 mL solutions of 5 mg/L, 25 mg/L, 50 mg/L, 75 mg/L and 100 mg/L concentration for 60 min at 25 °C (Table 3). But no appreciable increase in P_u was observed as the concentration of the Cr^{6+} ions increases in the solution. Maximum ion uptake of 29.31% was observed in solution with 100 mg/L concentration of Cr^{6+} ions. But remarkable increase in P_u (77.33%) and partition coefficient (3411.12) was observed in case of solution with 100 mg/L concentration of Fe^{2+} ions.

6.3. *Sorption studies as function of change in temperature*

Graft copolymers with maximum P_g were immersed in 100 mg/L concentrated solution of Fe^{2+} and Cr^{6+} ions at five different temperatures 25 °C, 30 °C, 35 °C, 40 °C and 45 °C (Table 3). The graft copolymers showed a slight increase in P_u when temperature was increased from 25 °C to 30 °C. 30.75% and 78.11% ion uptake was observed in solution containing Cr^{6+} and Fe^{2+} ions respectively at 30 °C. But with further increase in temperature the P_u decreases because of desorption at higher temperature.

7. Conclusions

The synthesized graft copolymers have been characterized physio-chemically by a variety of characterization techniques, confirming that VP has been grafted onto guar gum backbone. Because of formation of hydrogels in aqueous medium the graft copolymers can be investigated for their potential in metal ion sorption from water bodies. It has been observed from the foregone discussion that graft copolymers are effective sorbents for removal of Fe^{2+} ions than Cr^{6+} ions. Sorption of ions increases with increase in percent grafting and with increase in temperature desorption process cause decrease in sorption for both Fe^{2+} and Cr^{6+} ions.

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